

# UTILITY PATENT APPLICATION TRANSMITTAL

Only for new nonprovisional applications under 37 CFR § 1.53(b)

11-17-00 A  
Attorney Docket No. 2000U032.US

Inventors Sun-Chueh KAO and Parul A. Khokhani

Title A Method for Preparing A Catalyst Composition And Its Use  
In A Polymerization Process

Express Mail Label No. EL623902693US

PTO

71577447

11/16/00

## APPLICATION ELEMENTS

Assistant Commissioner for Patents  
ADDRESS TO:  
Box Patent Application  
Washington, D.C. 20231

1.  Fee Transmittal Form (e.g., PTO/SB/17)  
(Submit an original, and a duplicate for fee processing)

2.  Specification Total Pages 33  
(preferred arrangement set forth below)  
- Descriptive Title of the Invention  
- Cross References to Related Applications (if any)  
- Background of the Invention  
- Brief Summary of the Invention  
- Brief Description of the Drawings (if filed)  
- Detailed Description  
- Claim(s)  
- Abstract of the Disclosure

3.  Drawing(s) (35 U.S.C. 113) Total Sheets -0-

4.  Oath or Declaration Total Pages -2-  
(unsigned)  
a.  Newly executed (original or copy)  
b.  Copy from a prior application (37 C.F.R. § 1.63(d))  
(for continuation/division with Box 15 completed)  
[Note Box 5 below]  
i.  DELETION OF INVENTOR(S)  
Signed statement attached deleting  
inventor(s) named in the prior application,  
see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b).

5.  Incorporation By Reference (useable if Box 4B is checked)  
The entire disclosure of the prior application, from which a copy of the oath or declaration  
is supplied under Box 4b, is considered to be part of the disclosure of the accompanying  
application and is hereby incorporated by reference therein.

6.  Microfiche Computer Program (Appendix)

**ACCOMPANYING APPLICATION PARTS**

7.  Assignment Papers (cover sheet & document(s))

8.  37 C.F.R. § 3.73(b) Statement  Power of Attorney  
(when there is an assignee)

9.  English Translation Document (if applicable)

10.  Information Disclosure Statement (IDS)/PTO-1449  
 Copies of IDS Citations

11.  Preliminary Amendment

12.  Return Receipt Postcard (MPEP 503)  
(Should be specifically itemized)

13.  Certified Copy of Priority Document(s)  
(if foreign priority is claimed)

14.  Other:

15. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment.

Continuation  Divisional  Continuation-in-part (CIP)

of prior applications No: \_\_\_\_\_, from which priority is claimed under 35 U.S.C. § 120

Prior application information: Examiner \_\_\_\_\_ Group Art Unit \_\_\_\_\_

16. If a NONPROVISIONAL APPLICATION based upon a foreign or U.S. provisional application, priority is claimed from applications

No. \_\_\_\_\_, country \_\_\_\_\_, filed on \_\_\_\_\_.

## 17. CORRESPONDENCE ADDRESS

Customer Number or Bar Code Label

or  Correspondence address below

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Signature			Date	November 16, 2000	

# FEE TRANSMITTAL

Note: Effective December 29, 1999.  
Patent fees are subject to annual revision.

Total Amount of Payment **(\$728.00)**

## METHOD OF PAYMENT (check one)

The Commissioner is hereby authorized to charge indicated fees and credit any over payment to:

Deposit Account Number: **50-0589**

Deposit Account Name: **Univation Technologies, LLC**

Charge Any Additional Fee Required Under 37 CFR 1.16 and 1.17  
 Charge the Issue Fee Set in 37 CFR 1.18 at the Mailing of the Notice of Allowance

## FEE CALCULATION

### 1. FILING FEE

Large Entity Fee Code	Fee Description	Fee \$	Fee Paid
101	710 Utility filing fee		<b>710.00</b>
106	320 Design filing fee		
107	490 Plant filing fee		
108	710 Reissue filing fee		
114	150 Provisional filing fee		
<b>SUBTOTAL (1)</b>			<b>710.00</b>

### 2. CLAIMS

	Extra	Fee from below	Fee Paid
Total Claims	<b>21</b>	<b>1</b>	<b>18.00</b>
Independent Claims	<b>3</b>	<b>0</b>	<b>0.00</b>
Multiple Dependent Claims	<b>0</b>	<b>270.00</b>	<b>0.00</b>

### Large Entity

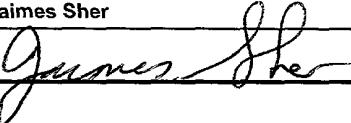
Fee Code	Fee \$	Fee Description
103	18	Claims in excess of 20
102	80	Independent claims in excess of 3
104	270	Multiple dependent claim
109	80	Reissue independent claims over original patent
110	18	Reissue claims in excess of 20 and over original patent
<b>SUBTOTAL (2)</b>		<b>18.00</b>

Complete if Known	
Application Number	New Application
Filing Date	November 16, 2000
Inventors	Sun-Chueh Kao and Parul A. Khokhani
Group Art Unit	Unassigned
Examiner Name	Unassigned
Attorney Docket Number	2000U032.US

## FEE CALCULATION (continued)

### 3. ADDITIONAL FEES

Fee Code	Large Entity Fee \$	Fee Description	FEES PAID
105	130	Surcharge – late filing fee or oath	
127	50	Surcharge – late provisional filing or cover sheet	
139	130	Non-English specification	
147	2,520	For filing a request for reexamination	
112	920*	Requesting publication of SIR prior to Examiner action	
113	1,840*	Requesting publication of SIR after Examiner action	
115	110	Extension for reply within first month	
116	380	Extension for reply within second month	
117	870	Extension for reply within third month	
118	1,360	Extension for reply within fourth month	
128	1,850	Extension for reply within fifth month	
119	300	Notice of Appeal	
120	300	Filing a brief in support of an appeal	
121	260	Request for oral hearing	
138	1,510	Petition to institute a public use proceeding	
140	110	Petition to revive – unavoidable	
141	1,210	Petition to revive – unintentional	
142	1,210	Utility issue fee (or reissue)	
143	430	Design issue fee	
144	580	Plant issue fee	
122	130	Petition to the Commissioner	
123	50	Petitions related to provisional applications	
126	240	Submission of information Disclosure Stmt.	
581	40	Recording each patent assignment per property (times number of properties)	
146	760	Filing a submission after final rejection (37 CFR 1.129(a))	
149	760	For each additional invention to be examiner (37 CFR 1.129(b))	
Other fee (specify)			
* Reduced by Basic Filing Fee Paid			
<b>SUBTOTAL (3)</b>			<b>.00</b>

Typed or Printed Name	Jaimes Sher	Reg. No.	34,726
Signature		Date	November 16, 2000

**NEW PATENT APPLICATION COVER PAGE**

**TITLE: A METHOD FOR PREPARING A CATALYST COMPOSITION AND ITS USE IN A POLYMERIZATION PROCESS**

**ATTY. DOCKET: 2000U032.US**

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**A METHOD FOR PREPARING A CATALYST  
COMPOSITION AND ITS USE IN A POLYMERIZATION PROCESS**

**5 FIELD OF THE INVENTION**

The present invention relates to a method for preparing a catalyst composition and for its use in a process for polymerizing olefin(s). In particular, the invention is directed to a method for preparing a catalyst composition of a supported activator and a catalyst compound and ionizing activator. More 10 specifically, the invention is directed to a catalyst composition of a supported activator, a Group 15 containing transition metal catalyst compound and a Group 13 containing ionizing activator.

**BACKGROUND OF THE INVENTION**

15 Advances in polymerization and catalysis have resulted in the capability to produce many new polymers having improved physical and chemical properties useful in a wide variety of superior products and applications. With the development of new catalysts the choice of polymerization-type (solution, slurry, high pressure or gas phase) for producing a particular polymer has greatly 20 expanded. Also, advances in polymerization technology have provided more efficient, highly productive and economically enhanced processes. Especially illustrative of these advances is the development of technology utilizing bulky ligand metallocene catalyst systems. In particular, in a slurry or gas phase process where typically a supported catalyst system is used, there are a variety of different 25 methods described in the art for supporting bulky ligand metallocene catalyst systems.

More recently, developments have lead to the discovery of anionic, multidentate heteroatom ligands as discussed by the following articles: (1) Kempe et al., "Aminopyridinato Ligands - New Directions and Limitations", 80<sup>th</sup> 30 Canadian Society for Chemistry Meeting, Windsor, Ontario, Canada, June 1-4, 1997; (2) Kempe et al., *Inorg. Chem.* 1996 vol 35 6742; (3) Jordan *et al.* of polyolefin catalysts based on hydroxyquinolines (Bei, X.; Swenson, D. C.; Jordan, R. F., *Organometallics* 1997, 16, 3282); (4) Horton, et.al., "Cationic 35 Alkylzirconium Complexes Based on a Tridentate Diamide Ligand: New Alkene Polymerization Catalysts", *Organometallics*, 1996, 15, 2672-2674 relates to tridentate zirconium complexes; (5) Baumann, et al., "Synthesis of Titanium and

Zirconium Complexes that Contain the Tridentate Diamido Ligand  $[(t\text{-Bu-d}_6\text{N})\text{O}\text{C}_6\text{H}_4\text{O}]^{2-}\{[\text{NON}]^{2-}\}$  and the Living Polymerization of 1-Hexene by Activated  $[\text{NON}]\text{ZrMe}_2$ ", Journal of the American Chemical Society, Vol. 119, pp. 3830-3831; (6) Cloke et al., "Zirconium Complexes incorporating the New Tridentate Diamide Ligand  $[(\text{Me}_3\text{Si})\text{N}\{\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_3)\}_2]^{2-}(\text{L})$ ; the Crystal Structure of  $[\text{Zr}(\text{BH}_4)_2\text{L}]$  and  $[\text{ZrCl}\{\text{CH}(\text{SiMe}_3)_2\}\text{L}]$ ", J. Chem. Soc. Dalton Trans, pp. 25-30, 1995; (7) Clark et al., "Titanium (IV) complexes incorporating the aminodiamide ligand  $[(\text{SiMe}_3)\text{N}\{\text{CH}_2\text{CH}_2\text{N}(\text{SiMe}_3)\}_2]^{2-}(\text{L})$ ; the X-ray crystal structure of  $[\text{TiMe}_2(\text{L})]$  and  $[\text{TiCl}\{\text{CH}(\text{SiMe}_3)_2\}(\text{L})]$ ", Journal of Organometallic Chemistry, Vol 50, pp. 333-340, 1995; (8) Scollard et al., "Living Polymerization of alpha-olefins by Chelating Diamide Complexes of Titanium", J. Am. Chem. Soc., Vol 118, No. 41, pp. 10008-10009, 1996; and (9) Guerin et al., "Conformationally Rigid Diamide Complexes: Synthesis and Structure of Titanium (IV) Alkyl Derivatives", Organometallics, Vol 15, No. 24, pp. 5085-5089, 1996.

15 Furthermore, U.S. Patent No. 5,576,460 describes a preparation of arylamine ligands and U.S. Patent No. 5,889,128 discloses a process for the living polymerization of olefins using initiators having a metal atom and a ligand having two group 15 atoms and a group 16 atom or three group 15 atoms. EP 893 454 A1 also describes preferably titanium transition metal amide compounds. In 20 addition, U.S. Patent No. 5,318,935 discusses amido transition metal compounds and catalyst systems especially for the producing isotactic polypropylene. Polymerization catalysts containing bidentate and tridentate ligands are further discussed in U.S. Patent No. 5,506,184.

25 Additionally, in U.S. Application Serial No. 09/460,179, filed December 10, 1999 describes Group 15 catalyst compounds used in combination with an aluminum containing ionizing activator. U.S. Application Serial No. 09/425,390 filed October 22, 1999 describes the use of a Group 15 catalyst compound in combination with a bulky ligand metallocene catalyst compound. While these 30 Group 15 containing catalyst compounds are useful, a need exists in the industry to improve the commercial viability of these new catalyst developments.

35 There are a variety of techniques discussed for preparing a supported activator and to its use in a catalyst system for polymerizing olefin(s), mostly where the catalyst compounds are bulky ligand metallocene catalyst compounds. The following non-limiting examples of patent publications discussing supported activators, which are all fully incorporated herein by reference, include: U.S.

Patent No. 5,728,855 directed to the forming a supported oligomeric alkylaluminoxane formed by treating a trialkylaluminum with carbon dioxide prior to hydrolysis; U.S. Patent Nos. 5,831,109 and 5,777,143 discusses a supported methylalumoxane made using a non-hydrolytic process; U.S. Patent 5 No. 5,731,451 relates to a process for making a supported alumoxane by oxygenation with a trialkylsiloxy moiety; U.S. Patent No. 5,856,255 discusses forming a supported auxiliary catalyst (alumoxane or organoboron compound) at elevated temperatures and pressures; U.S. Patent No. 5,739,368 discusses a process of heat treating alumoxane and placing it on a support; EP-A-0 545 152 10 relates to adding a metallocene to a supported alumoxane and adding more methylalumoxane; U.S. Patent Nos. 5,756,416 and 6,028,151 discuss a catalyst composition of a alumoxane impregnated support and a metallocene and a bulky aluminum alkyl and methylalumoxane; EP-B1-0 662 979 discusses the use of a metallocene with a catalyst support of silica reacted with alumoxane; PCT WO 15 96/16092 relates to a heated support treated with alumoxane and washing to remove unfixed alumoxane; U.S. Patent Nos. 4,912,075, 4,937,301, 5,008,228, 5,086,025, 5,147,949, 4,871,705, 5,229,478, 4,935,397, 4,937,217 and 5,057,475, and PCT WO 94/26793 all directed to adding a metallocene to a supported activator; U.S. Patent No. 5,902,766 relates to a supported activator having a 20 specified distribution of alumoxane on the silica particles; U.S. Patent No. 5,468,702 relates to aging a supported activator and adding a metallocene; U.S. Patent No. 5,968,864 discusses treating a solid with alumoxane and introducing a metallocene; EP 0 747 430 A1 relates to a process using a metallocene on a supported methylalumoxane and trimethylaluminum; EP 0 969 019 A1 discusses the use of a metallocene and a supported activator; EP-B2-0 170 059 relates to a 25 polymerization process using a metallocene and a organo-aluminuim compound, which is formed by reacting aluminum trialkyl with a water containing support; U.S. Patent No. 5,212,232 discusses the use of a supported alumoxane and a metallocene for producing styrene based polymers; U.S. Patent No. 5,026,797 30 discusses a polymerization process using a solid component of a zirconium compound and a water-insoluble porous inorganic oxide preliminarily treated with alumoxane; U.S. Patent No. 5,910,463 relates to a process for preparing a catalyst support by combining a dehydrated support material, an alumoxane and a polyfunctional organic crosslinker; U.S. Patent Nos. 5,332,706, 5,473,028, 35 5,602,067 and 5,420,220 discusses a process for making a supported activator

where the volume of alumoxane solution is less than the pore volume of the support material; WO 98/02246 discusses silica treated with a solution containing a source of aluminum and a metallocene; WO 99/03580 relates to the use of a supported alumoxane and a metallocene; EP-A1-0 953 581 discloses a 5 heterogeneous catalytic system of a supported alumoxane and a metallocene; U.S. Patent No. 5,015,749 discusses a process for preparing a polyhydrocarbyl-alumoxane using a porous organic or inorganic imbibing material; U.S. Patent Nos. 5,446,001 and 5,534,474 relates to a process for preparing one or more alkylaluminoxanes immobilized on a solid, particulate inert support; and EP-A1-0 10 819 706 relates to a process for preparing a solid silica treated with alumoxane. Also, the following articles, also fully incorporated herein by reference for purposes of disclosing useful supported activators and methods for their preparation, include: W. Kaminsky, et al., "Polymerization of Styrene with Supported Half-Sandwich Complexes", Journal of Polymer Science Vol. 37, 15 2959-2968 (1999) describes a process of adsorbing a methylalumoxane to a support followed by the adsorption of a metallocene; Junting Xu, et al. "Characterization of isotactic polypropylene prepared with dimethylsilyl bis(1-indenyl)zirconium dichloride supported on methylaluminoxane pretreated silica", European Polymer Journal 35 (1999) 1289-1294, discusses the use of silica treated 20 with methylalumoxane and a metallocene; Stephen O'Brien, et al., "EXAFS analysis of a chiral alkene polymerization catalyst incorporated in the mesoporous silicate MCM-41" Chem. Commun. 1905-1906 (1997) discloses an immobilized alumoxane on a modified mesoporous silica; and F. Bonini, et al., "Propylene Polymerization through Supported Metallocene/MAO Catalysts: Kinetic Analysis 25 and Modeling" Journal of Polymer Science, Vol. 33 2393-2402 (1995) discusses using a methylalumoxane supported silica with a metallocene.

Also, combination of activators have been described in for example, U.S. Patent Nos. 5,153,157 and 5,453,410, European publication EP-B1 0 573 120, and PCT publications WO 94/07928 and WO 95/14044. These documents all discuss the 30 use of an alumoxane and an ionizing activator with a bulky ligand metallocene catalyst compound.

While all these methods have been described in the art, a need for an improved method for preparing a catalyst composition utilizing Group 15 containing catalyst compounds has been discovered.

## **SUMMARY OF THE INVENTION**

This invention provides for a catalyst system and for its use in a polymerizing process.

In one embodiment, the invention relates to a method for making a catalyst 5 composition comprising the steps of: (a) forming a supported activator; (b) introducing a Group 15 containing catalyst compound; and (c) introducing an ionizing activator.

In another embodiment the invention is directed to a catalyst composition 10 of a supported activator, a Group 15 containing compound and an ionizing activator, preferably where the ionizing activator is a Group 13 containing ionizing activator.

In an embodiment, the invention is directed to forming a catalyst 15 composition of a Group 15 containing bidentate or tridentate ligated transition metal catalyst compound, a supported activator comprising the product of combining a support material and an activator, and an ionizing activator, and to its use in the polymerization of olefin(s). In the most preferred embodiment, the activator is an aluminum containing compound and the ionizing activator is a boron containing compound.

In another embodiment, the invention is directed to a catalyst composition 20 of a catalyst compound having a transition metal bound to at least one leaving group and also bound to at least two Group 15 atoms, at least one of which is also bound to a Group 15 or 16 atom through another group, a supported activator, preferably a supported alumoxane, and an ionizing activator, and to its use in the polymerization of olefin(s).

25 In another embodiment, the invention is directed to a process for polymerizing olefin(s), particularly in a gas phase or slurry phase process, utilizing any one of the catalyst compositions discussed above.

## **DETAILED DESCRIPTION OF THE INVENTION**

### **Introduction**

30 It has been found that the catalyst composition of the invention which includes a supported activator, at least one Group 15 containing transition metal catalyst compound, and an ionizing activator having higher commercially acceptable activities. Also, the catalyst composition of the invention has a higher comonomer incorporation rate when utilized in the polymerization of one or more 35

olefin(s). Furthermore, the catalyst composition of the invention, in one particular embodiment, is useful in a slurry form, thus not requiring the need to remove all liquids involved in forming a traditional supported catalyst system.

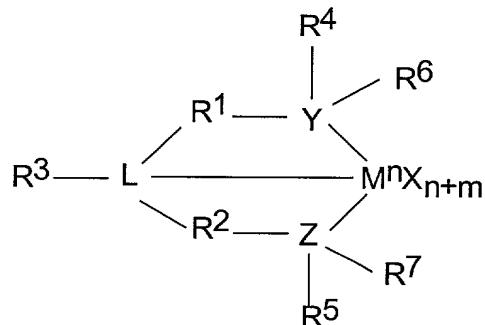
**Group 15 containing Metal Catalyst Compound and Catalyst Systems**

5 In one embodiment, the metal based catalyst compounds utilized in the catalyst composition of the invention are Group 15 bidentate or tridentate ligated transition metal compound having at least one substituted hydrocarbon group, the preferred Group 15 elements are nitrogen and/or phosphorous, most preferably nitrogen, and the preferred leaving group is a substituted alkyl group having  
10 greater than 6 carbon atoms, preferably the alkyl substituted with an aryl group.

The Group 15 containing metal catalyst compounds of the invention generally include a transition metal atom bound to at least one substituted hydrocarbon leaving group and also bound to at least two Group 15 atoms, at least one of which is also bound to a Group 15 or 16 atom through another group.

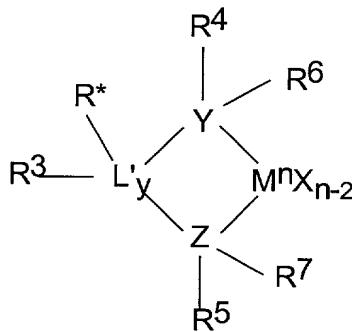
15 In one preferred embodiment, at least one of the Group 15 atoms is also bound to a Group 15 or 16 atom through another group, which may be a hydrocarbon group, preferably a hydrocarbon group having 1 to 20 carbon atoms, a heteroatom containing group, preferably silicon, germanium, tin, lead, or phosphorus. In this embodiment, it is further preferred that the Group 15 or 16  
20 atom be bound to nothing or a hydrogen, a Group 14 atom containing group, a halogen, or a heteroatom containing group. Additionally in these embodiment, it is preferred that each of the two Group 15 atoms are also bound to a cyclic group that may optionally be bound to hydrogen, a halogen, a heteroatom or a hydrocarbyl group, or a heteroatom containing group.

25 In an embodiment of the invention, the Group 15 containing metal compound of the invention is represented by the formulae:



Formula (I)

or



Formula (II)

wherein M is a metal, preferably a transition metal, more preferably a Group 4,5 or 6 metal, even more preferably a Group 4 metal, and most preferably hafnium or zirconium; each X is independently a leaving group, preferably, an anionic leaving group, and more preferably hydrogen, a hydrocarbyl group, a heteroatom, and most preferably an alkyl. In a most preferred embodiment, at least one X is a substituted hydrocarbon group, preferably a substituted alkyl group having more than 6 carbon atoms, more preferably an aryl substituted alkyl group and most preferably a benzyl group.

5 y is 0 or 1 (when y is 0 group L' is absent);

n is the oxidation state of M, preferably +2, +3, +4 or +5 and more preferably +4;

m is the formal charge of the YZL or the YZL' ligand, preferably 0, -1, -2 or -3, and more preferably -2;

10 L is a Group 15 or 16 element, preferably nitrogen;

L' is a Group 15 or 16 element or Group 14 containing group, preferably carbon, silicon or germanium;

15 Y is a Group 15 element, preferably nitrogen or phosphorus, and more preferably nitrogen;

Z is a Group 15 element, preferably nitrogen or phosphorus, and more preferably nitrogen;

20 R<sup>1</sup> and R<sup>2</sup> are independently a C<sub>1</sub> to C<sub>20</sub> hydrocarbon group, a heteroatom containing group having up to twenty carbon atoms, silicon, germanium, tin, lead, or phosphorus, preferably a C<sub>2</sub> to C<sub>20</sub> alkyl, aryl or arylalkyl group, more preferably a linear, branched or cyclic C<sub>2</sub> to C<sub>20</sub> alkyl group, most preferably a C<sub>2</sub> to C<sub>6</sub> hydrocarbon group;

R<sup>3</sup> is absent or a hydrocarbon group, hydrogen, a halogen, a heteroatom containing group, preferably a linear, cyclic or branched alkyl group having 1 to 20 carbon atoms, more preferably R<sup>3</sup> is absent, hydrogen or an alkyl group, and most preferably hydrogen;

5 R<sup>4</sup> and R<sup>5</sup> are independently an alkyl group, an aryl group, substituted aryl group, a cyclic alkyl group, a substituted cyclic alkyl group, a cyclic arylalkyl group, a substituted cyclic arylalkyl group or multiple ring system, preferably having up to 20 carbon atoms, more preferably between 3 and 10 carbon atoms, and even more preferably a C<sub>1</sub> to C<sub>20</sub> hydrocarbon group, a C<sub>1</sub> to C<sub>20</sub> aryl group or a C<sub>1</sub> to C<sub>20</sub>

10 arylalkyl group, or a heteroatom containing group, for example PR<sub>3</sub>, where R is an alkyl group;

R<sup>1</sup> and R<sup>2</sup> may be interconnected to each other, and/or R<sup>4</sup> and R<sup>5</sup> may be interconnected to each other;

15 R<sup>6</sup> and R<sup>7</sup> are independently absent, or hydrogen, an alkyl group, halogen, heteroatom or a hydrocarbyl group, preferably a linear, cyclic or branched alkyl group having 1 to 20 carbon atoms, more preferably absent; and

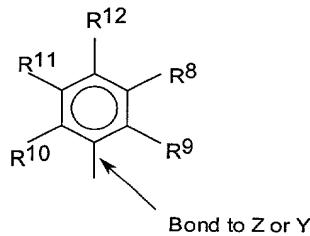
R\* is absent, or is hydrogen, a Group 14 atom containing group, a halogen, a heteroatom containing group.

20 By "formal charge of the YZL or YZL' ligand", it is meant the charge of the entire ligand absent the metal and the leaving groups X.

25 By "R<sup>1</sup> and R<sup>2</sup> may also be interconnected" it is meant that R<sup>1</sup> and R<sup>2</sup> may be directly bound to each other or may be bound to each other through other groups. By "R<sup>4</sup> and R<sup>5</sup> may also be interconnected" it is meant that R<sup>4</sup> and R<sup>5</sup> may be directly bound to each other or may be bound to each other through other groups.

30 An alkyl group may be a linear, branched alkyl radicals, or alkenyl radicals, alkynyl radicals, cycloalkyl radicals or aryl radicals, acyl radicals, aroyl radicals, alkoxy radicals, aryloxy radicals, alkylthio radicals, dialkylamino radicals, alkoxycarbonyl radicals, aryloxycarbonyl radicals, carbomoyl radicals, alkyl- or dialkyl- carbamoyl radicals, acyloxy radicals, acylamino radicals, aroylamino radicals, straight, branched or cyclic, alkylene radicals, or combination thereof. An arylalkyl group is defined to be a substituted aryl group.

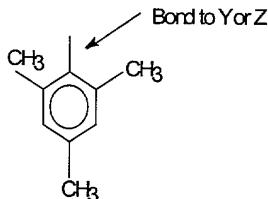
In a preferred embodiment R<sup>4</sup> and R<sup>5</sup> are independently a group represented by the following formula:



Formula (III)

wherein R<sup>8</sup> to R<sup>12</sup> are each independently hydrogen, a C<sub>1</sub> to C<sub>40</sub> alkyl group, a halide, a heteroatom, a heteroatom containing group containing up to 40 carbon atoms, preferably a C<sub>1</sub> to C<sub>20</sub> linear or branched alkyl group, preferably a methyl, ethyl, propyl or butyl group, any two R groups may form a cyclic group and/or a heterocyclic group. The cyclic groups may be aromatic. In a preferred embodiment R<sup>9</sup>, R<sup>10</sup> and R<sup>12</sup> are independently a methyl, ethyl, propyl or butyl group (including all isomers), in a preferred embodiment R<sup>9</sup>, R<sup>10</sup> and R<sup>12</sup> are methyl groups, and R<sup>8</sup> and R<sup>11</sup> are hydrogen.

10 In a particularly preferred embodiment R<sup>4</sup> and R<sup>5</sup> are both a group represented by the following formula:



Formula (IV)

15 In this embodiment, M is hafnium or zirconium; each of L, Y, and Z is nitrogen; each of R<sup>1</sup> and R<sup>2</sup> is a hydrocarbyl group, preferably -CH<sub>2</sub>-CH<sub>2</sub>-; R<sup>3</sup> is hydrogen; and R<sup>6</sup> and R<sup>7</sup> are absent.

The Group 15 containing metal catalyst compounds utilized in the catalyst 20 composition of the invention are prepared by methods known in the art, such as those disclosed in EP 0 893 454 A1, U.S. Patent No. 5,889,128 and the references cited in U.S. Patent No. 5,889,128 which are all herein incorporated by reference. U.S. Application Serial Number 09/312,878, filed May 17, 1999, discloses a gas 25 or slurry phase polymerization process using a supported bisamide catalyst, which is also incorporated herein by reference. A preferred direct synthesis of these compounds comprises reacting the neutral ligand, (see for example YZL or YZL' of Formula I or II) with MX<sub>n</sub>, n is the oxidation state of the metal, each X is an

anionic group, such as halide, in a non-coordinating or weakly coordinating solvent, such as ether, toluene, xylene, benzene, methylene chloride, and/or hexane or other solvent having a boiling point above 60°C, at about 20°C to about 150°C (preferably 20°C to 100°C), preferably for 24 hours or more, then treating 5 the mixture with an excess (such as four or more equivalents) of an alkylating agent, such as methyl magnesium bromide in ether. The magnesium salts are removed by filtration, and the metal complex isolated by standard techniques.

In one embodiment the Group 15 containing metal catalyst compound is prepared by a method comprising reacting a neutral ligand, (see for example YZL 10 or YZL' of formula 1 or 2) with a compound represented by the formula  $MX_n$  (where n is the oxidation state of M, M is a transition metal, and each X is an anionic leaving group) in a non-coordinating or weakly coordinating solvent, at about 20°C or above, preferably at about 20°C to about 100°C, then treating the mixture with an excess of an alkylating agent, then recovering the metal complex. 15

In a preferred embodiment the solvent has a boiling point above 60°C, such as toluene, xylene, benzene, and/or hexane. In another embodiment the solvent comprises ether and/or methylene chloride, either being preferable.

In one embodiment, two or more Group 15 containing compounds as discussed above are used in combination with a supported activator and an 20 ionizing activator.

In yet another embodiment, the Group 15 containing catalyst compounds of the invention are combined with one or a combination of the following catalyst compounds: (1) those catalyst compounds having bidentate ligands containing pyridine or quinoline moieties, such as those described in 25 U.S. Application Serial No. 09/103,620 filed June 23, 1998, or those bulky ligands described in PCT publications WO 99/01481 and WO 98/42664, which are fully incorporated herein by reference; (2) those catalyst compounds of  $Ni^{2+}$  and  $Pd^{2+}$  described in the articles Johnson, et al., "New Pd(II)- and Ni(II)- Based Catalysts for Polymerization of Ethylene and a- 30 Olefins", J. Am. Chem. Soc. 1995, 117, 6414-6415 and Johnson, et al., "Copolymerization of Ethylene and Propylene with Functionalized Vinyl Monomers by Palladium(II) Catalysts", J. Am. Chem. Soc., 1996, 118, 267- 268, and WO 96/23010 published August 1, 1996, WO 99/02472, U.S. Patent 35 Nos. 5,852,145, 5,866,663 and 5,880,241, which are all herein fully incorporated by reference; (3) those catalyst compounds of diimine based

ligands of Group 8 to 10 metal compounds as disclosed in PCT publications WO 96/23010, WO 97/48735 and WO 98/40374 and Gibson, et. al., *Chem. Comm.*, pp. 849-850 (1998), all of which are herein incorporated by reference; (4) those catalyst compounds that are traditional metallocene catalysts as described in U.S. Patent Nos. 5,324,800, 5,064,802, 5,145,819, 5,149,819, 5,243,001, 5,239,022, 5,276,208, 5,296,434, 5,057,475, 5,096,867, 5,055,438, 5,198,401, 5,227,440, 5,264,405, 5,321,106, 5,329,031, 5,304,614, 5,677,401, 5,723,398, 5,753,578, 5,854,363, 5,856,547 5,858,903, 5,859,158, 5,900,517, 5,939,503 and 5,962,718 and PCT publications WO 93/08221, 10 WO 93/08199, WO 92/00333, WO 94/07928, WO 91/04257, WO 94/03506, WO 96/00244, WO 97/15602, WO 99/20637, WO 95/07140, WO 98/11144, WO 98/41530, WO 98/41529, WO 98/46650, WO 99/02540 and WO 99/14221 and European publications EP-A-0 578 838, EP-A-0 638 595, EP-B-0 513 380, EP-A1-0 816 372, EP-A2-0 839 834, EP-A-0 420 436, EP-B1-0 15 632 819, EP-B1-0 739 361, EP-B1-0 748 821 and EP-B1-0 757 996, all of which are herein fully incorporated by reference; and (5) those traditional Ziegler-Natta catalysts and Phillips-type chromium catalyst well known in the art for example as discussed in U.S. Patent Nos. 4,115,639, 4,077,904 20 4,482,687, 4,564,605, 4,721,763, 4,879,359 and 4,960,741 all of which are herein fully incorporated by reference.

### Activators

For the purposes of this patent specification and appended claims, the term "activator" is defined to be any compound or component or method which can activate any of the catalyst compounds or combinations thereof of the invention 25 for the polymerization of olefin(s).

### Supported Activators

Many of the supported activators of the invention are described in the various patents and publications in the background of this patent specification, all of which are herein fully incorporated by reference. Any of the methods discussed 30 are useful for producing the supported activator component of the invention. In one embodiment, alumoxanes as activators are used in the supported activator of the invention. Alumoxanes are generally oligomeric compounds containing - Al(R)-O- subunits, where R is an alkyl group. Examples of alumoxanes include methylalumoxane (MAO), modified methylalumoxane (MMAO), 35 ethylalumoxane and isobutylalumoxane. Alumoxanes may be produced by the

hydrolysis of the respective trialkylaluminum compound. MMAO may be produced by the hydrolysis of trimethylaluminum and a higher trialkylaluminum such as triisobutylaluminum. MMAO's are generally more soluble in aliphatic solvents and more stable during storage. A variety of methods for preparing 5 alumoxanes and modified alumoxanes are described in U.S. Patent Nos. 4,665,208, 4,952,540, 5,091,352, 5,206,199, 5,204,419, 4,874,734, 4,924,018, 4,908,463, 4,968,827, 5,041,584, 5,308,815, 5,329,032, 5,248,801, 5,235,081, 5,157,137, 5,103,031, 5,391,793, 5,391,529, 5,693,838, 5,731,253, 5,731,451, 5,744,656, 5,847,177, 5,854,166, 5,856,256 and 5,939,346 and European 10 publications EP-A-0 561 476, EP-B1-0 279 586, EP-A-0 594-218 and EP-B1-0 586 665, and PCT publication WO 94/10180. Other alumoxanes include siloxy alumoxanes as described in EP-B1-0 621 279 and U.S. Patent No. 6,060,418, and chemically functionalized carboxylate-alumoxane described in WO 00/09578, which are herein incorporated by reference. 15 Other activators useful in forming the supported activator of the invention are aluminum alkyl compounds, such as trialkylaluminums and alkyl aluminum chlorides. Examples of these activators include trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum and the like. 20 The above-described activators may be combined with one or more support materials also described above using one or more support methods well known in the art. For example, in a most preferred embodiment, an activator is deposited on, contacted with, or incorporated within, vaporized onto, reacted with, adsorbed or absorbed in, or on, a support material. 25 The support material for forming the supported activator is any of the conventional support materials. Preferably the supported material is a porous support material, for example, talc, inorganic oxides and inorganic chlorides. Other support materials include resinous support materials such as polystyrene, functionalized or crosslinked organic supports, such as polystyrene divinyl 30 benzene polyolefins or polymeric compounds, zeolites, clays, or any other organic or inorganic support material and the like, or mixtures thereof. 35 The preferred support materials are inorganic oxides that include those Group 2, 3, 4, 5, 13 or 14 metal oxides. The preferred support materials include silica, alumina, silica-alumina, magnesium chloride, and mixtures thereof. Other useful support materials include magnesia, titania, zirconia, montmorillonite (EP-

B1 0 511 665), hydrotalcites, and the like. Also, combinations of these support materials may be used, for example, silica-chromium, silica-alumina, silica-titania and the like.

It is preferred that the support material, most preferably an inorganic oxide, has a surface area in the range of from about 10 to about 700 m<sup>2</sup>/g, pore volume in the range of from about 0.1 to about 4.0 cc/g and average particle size in the range of from about 5 to about 500 µm. More preferably, the surface area of the support material is in the range of from about 50 to about 500 m<sup>2</sup>/g, pore volume of from about 0.5 to about 3.5 cc/g and average particle size of from about 10 to about 200 µm. Most preferably the surface area of the support material is in the range is from about 100 to about 400 m<sup>2</sup>/g, pore volume from about 0.8 to about 3.0 cc/g and average particle size is from about 5 to about 100 µm. The average pore size of the carrier of the invention typically has pore size in the range of from 10 to 1000Å, preferably 50 to about 500Å, and most preferably 75 to about 350Å.

The support materials may be treated chemically, for example with a fluoride compound as described in WO 00/12565, which is herein incorporated by reference. Other supported activators are described in for example WO 00/13792 that refers to supported boron containing solid acid complex.

In a preferred method of forming the supported activator the amount of liquid in which the activator is present is in an amount that is less than four times the pore volume of the support material, more preferably less than three times, even more preferably less than two times; preferred ranges being from 1.1 times to 3.5 times range and most preferably in the 1.2 to 3 times range. In an alternative embodiment, the amount of liquid in which the activator is present is from one to less than one times the pore volume of the support material utilized in forming the supported activator.

Procedures for measuring the total pore volume of a porous support are well known in the art. Details of one of these procedures is discussed in Volume 30 1, *Experimental Methods in Catalytic Research* (Academic Press, 1968) (specifically see pages 67-96). This preferred procedure involves the use of a classical BET apparatus for nitrogen absorption. Another method well known in the art is described in Innes, *Total Porosity and Particle Density of Fluid Catalysts By Liquid Titration*, Vol. 28, No. 3, Analytical Chemistry 332-334 (March, 1956).

In an embodiment, the supported activator is in a dried state, a solid. In another embodiment, the supported activator is in a substantially dry state or a slurry, preferably in a mineral oil slurry.

5 In another embodiment, two or more separately supported activators are used, or alternatively, two or more different activators on a single support are used.

### **Ionizing Activators**

10 Ionizing activators of the invention, in one embodiment are those ionizing or stoichiometric activators, which are either neutral or ionic. For example ionizing activators include tri (n-butyl) ammonium tetrakis (pentafluorophenyl) boron, a trisperfluorophenyl boron metalloid precursor or a trisperfluoronaphthyl boron metalloid precursor, polyhalogenated heteroborane anions (WO 98/43983) or combination thereof, that would ionize the neutral catalyst compound. It is also 15 within the scope of this invention to use neutral and ionic ionizing activators in combination.

Examples of neutral stoichiometric ionizing activators include tri-substituted boron, tellurium, aluminum, gallium and indium or mixtures thereof. The three substituent groups are each independently selected from alkyls, alkenyls, halogen, substituted alkyls, aryls, arylhalides, alkoxy and halides.

20 Preferably, the three groups are independently selected from halogen, mono or multicyclic (including halosubstituted) aryls, alkyls, and alkenyl compounds and mixtures thereof, preferred are alkenyl groups having 1 to 20 carbon atoms, alkyl groups having 1 to 20 carbon atoms, alkoxy groups having 1 to 20 carbon atoms and aryl groups having 3 to 20 carbon atoms (including substituted aryls). More 25 preferably, the three groups are alkyls having 1 to 4 carbon groups, phenyl, napthyl or mixtures thereof. More preferably, the three groups are a fluorinated hydrocarbyl group having 1 to 20 carbon atoms, preferably a fluorinated aryl group, and more preferably a pentafluoryl aryl group. Most preferably, the neutral stoichiometric activator is trisperfluorophenyl boron or trisperfluoronaphthyl 30 boron.

Ionic stoichiometric ionizing activators, in one embodiment, contain an active proton, or some other cation associated with, but not coordinated to, or only loosely coordinated to, the remaining ion of the ionizing compound. Such compounds and the like are described in European publications EP-A-0 570 982, 35 EP-A-0 520 732, EP-A-0 495 375, EP-B1-0 500 944, EP-A-0 277 003 and EP-A-

0 277 004, and U.S. Patent Nos. 5,153,157, 5,198,401, 5,066,741, 5,206,197, 5,241,025, 5,384,299 and 5,502,124 and U.S. Patent Application Serial No. 08/285,380, filed August 3, 1994, all of which are herein fully incorporated by reference.

5 In a preferred embodiment, the ionizing activators include a cation and an anion component, and is represented by the following formula:



10 wherein  $L'''$  is a neutral Lewis base;

H is hydrogen;

$(L'''-H)^+$  is a Bronsted acid

$A^{d-}$  is a non-coordinating anion having the charge  $d-$

d is an integer from 1 to 3.

15

The cation component,  $(L'''-H)_d^+$  may include Bronsted acids such as protons or protonated Lewis bases or reducible Lewis acids capable of protonating or abstracting a moiety, such as an alkyl or aryl, from the catalysts compound of the invention, in particular the Group 15 containing transition metal catalyst compound, resulting in a cationic transition metal species.

20 The activating cation  $(L'''-H)_d^+$  may be a Bronsted acid, capable of donating a proton to the transition metal catalytic precursor resulting in a transition metal cation, including ammoniums, oxoniums, phosphoniums, silyliums and mixtures thereof, preferably ammoniums of methylamine, aniline, dimethylamine, diethylamine, N-methylaniline, diphenylamine, trimethylamine, 25 triethylamine, N,N-dimethylaniline, methyl diphenylamine, pyridine, p-bromo N,N-dimethylaniline, p-nitro-N,N-dimethylaniline, phosphoniums from triethylphosphine, triphenylphosphine, and diphenylphosphine, oxoniums from ethers such as dimethyl ether diethyl ether, tetrahydrofuran and dioxane, 30 sulfoniums from thioethers, such as diethyl thioethers and tetrahydrothiophene and mixtures thereof. The activating cation  $(L'''-H)_d^+$  may also be an abstracting moiety such as silver, carboniums, tropylum, carbeniums, ferroceniums and mixtures, preferably carboniums and ferroceniums. Most preferably  $(L'''-H)_d^+$  is triphenyl carbonium.

The anion component  $A^{d-}$  include those having the formula  $[M^{k+}Q_n]^{d-}$  wherein k is an integer from 1 to 3; n is an integer from 2-6;  $n - k = d$ ; M is an element selected from Group 13 of the Periodic Table of the Elements and Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, 5 aryloxide, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, and halosubstituted-hydrocarbyl radicals, said Q having up to 20 carbon atoms with the proviso that in not more than 1 occurrence is Q a halide. Preferably, each Q is a fluorinated hydrocarbyl group having 1 to 20 carbon atoms, more preferably each Q is a fluorinated aryl group, and most preferably 10 each Q is a pentafluoryl aryl group. Examples of suitable  $A^{d-}$  also include diboron compounds as disclosed in U.S. Pat. No. 5,447,895, which is fully incorporated herein by reference.

Most preferably, the ionic stoichiometric activator  $(L'''-H)_d^+ (A^{d-})$  is N,N-dimethylanilinium tetra(perfluorophenyl)borate or triphenylcarbenium 15 tetra(perfluorophenyl)borate.

Other activators include those described in PCT publication WO 98/07515 such as tris (2, 2', 2"- nonafluorobiphenyl) fluoroaluminate, which publication is fully incorporated herein by reference. WO 98/09996 incorporated herein by reference describes activating metal compounds with perchlorates, periodates and 20 iodates including their hydrates. WO 98/30602 and WO 98/30603 incorporated by reference describe the use of lithium (2,2'-bisphenyl-dtrimethylsilicate)•4THF as an activator. EP-A2-0 103 675 describes fluorinated organic compound activators, which is herein incorporated by reference. WO 99/18135 incorporated herein by reference describes the use of organo-boron-aluminum activators. EP-25 B1-0 781 299 describes using a silylum salt in combination with a non-coordinating compatible anion. Other activators are described in for example, U.S. Patent Nos. 5,849,852, 5,859,653, 5,869,723 and 6,030,917 (gallium based anion activators) and PCT WO 98/32775, WO 00/09513 (three coordinate aluminum activator) and WO 00/20115, which are all herein incorporated by reference.

30

### Catalyst Composition

The catalyst composition of the invention is formed in various ways. In one embodiment, a supported activator is combined with a Group 15 transition metal compound and an ionizing activator, preferably in mineral oil.

In a preferred embodiment, the resulting mixture of the combination of the supported activator, Group 15 transition metal catalyst compound and the ionizing activator is stirred for a period of time and at a specified temperature. In one embodiment, the mixing time is in the range of from 1 minute to several days, 5 preferably about one hour to about a day, more preferably from about 2 hours to about 20 hours, and most preferably from about 5 hours to about 16 hours. The period of contacting refers to the mixing time only.

The mixing temperature ranges from -60 °C to about 200°C, preferably from 0°C to about 100°C, more preferably from about 10°C to about 60°C, still 10 more preferably from 20°C to about 40°C, and most preferably at room temperature.

In general the Group 15 transition metal catalyst compound and supported activator, for example in the preferred embodiment, where the supported activator is a supported aluminum compound, most preferably alumoxane, the ratio of 15 aluminum atom to catalyst transition metal atom is about 1000:1 to about 1:1, preferably a ratio of about 300:1 to about 1:1, and more preferably about 50:1 to about 250:1, and most preferably from 100:1 to 125:1.

In another embodiment, the ionizing activator compound is utilized in a quantity that provides a mole ratio of the ionizing activator to the catalyst 20 transition metal atom of from about 0.01 to 1.0, preferably from about 0.1 to about 0.9, more preferably from 0.2 to about 0.8 and most preferably from about 0.3 to 0.7.

In another embodiment the combined amount in weight percent of the supported activator to the Group 15 containing transition metal compound and the 25 ionizing compound are in the range of from 99.9 weight percent to 50 weight percent, preferably from about 99.8 weight percent to about 60 weight percent, more preferably from about 99.7 weight percent to about 70 weight percent, and most preferably from about 99.6 weight percent to about 80 weight percent.

In other embodiments of the invention the supported activator is in a dry or 30 substantially dried state, or in a solution, when contacted with the Group 15 containing transition metal catalyst and the ionizing activator. In this embodiment, the resulting catalyst composition is used in a dry or substantially dry state, or as a slurry, in preferably a mineral oil. Also, the dried catalyst composition of the invention can be reslurried in a liquid such as mineral oil, toluene, or any the 35 hydrocarbon prior to its introduction into a polymerization reactor.

Furthermore, it is contemplated that the supported activator, Group 15 containing catalyst compound and the ionizing activator can be used in the same solvents or different solvents. For example, the catalyst compound can be in toluene, the ionizing activator in isopentane and the supported activator in mineral oil, or any combination of solvents. In the most preferred embodiment, the solvent is the same, and is most preferably a mineral oil.

Antistatic agents or surface modifiers may be used in combination with the supported activator, Group 15 containing catalyst compound and ionizing activator, see for example those agents and modifiers described in PCT publication WO 96/11960, which is herein fully incorporated by reference. Also, a carboxylic acid salt of a metal ester, for example aluminum carboxylates such as aluminum mono, di- and tri- stearates, aluminum octoates, oleates and cyclohexylbutyrates, as described in U.S. Application Serial No. 09/113,216, filed July 10, 1998 may be used in combination with a supported activator, Group 15 containing catalyst compound and ionizing activator.

In one embodiment of the invention, olefin(s), preferably C<sub>2</sub> to C<sub>30</sub> olefin(s) or alpha-olefin(s), preferably ethylene or propylene or combinations thereof are prepolymerized in the presence of the supported activator, Group 15 containing catalyst compound and ionizing activator combination prior to the main polymerization. The prepolymerization can be carried out batchwise or continuously in gas, solution or slurry phase including at elevated pressures. The prepolymerization can take place with any olefin monomer or combination and/or in the presence of any molecular weight controlling agent such as hydrogen. For examples of prepolymerization procedures, see U.S. Patent Nos. 4,748,221, 4,789,359, 4,923,833, 4,921,825, 5,283,278 and 5,705,578 and European Publication EP-B1-0 279 863 and PCT Publication WO 97/44371, and all of which are herein fully incorporated by reference.

### **Polymerization Process**

The catalyst composition of the invention described above are suitable for use in any polymerization process over a wide range of temperatures and pressures. The temperatures may be in the range of from -60 °C to about 280°C, preferably from 50°C to about 200°C, and the pressures employed may be in the range from 1 atmosphere to about 500 atmospheres or higher.

Polymerization processes include solution, gas phase, slurry phase and a high pressure process or a combination thereof. Particularly preferred is a gas

phase or slurry phase polymerization of one or more olefin(s) at least one of which is ethylene or propylene.

In one embodiment, the process of this invention is directed toward a solution, high pressure, slurry or gas phase polymerization process of one or more olefin monomers having from 2 to 30 carbon atoms, preferably 2 to 12 carbon atoms, and more preferably 2 to 8 carbon atoms. The invention is particularly well suited to the polymerization of two or more olefin monomers of ethylene, propylene, butene-1, pentene-1, 4-methyl-pentene-1, hexene-1, octene-1 and decene-1.

Other monomers useful in the process of the invention include ethylenically unsaturated monomers, diolefins having 4 to 18 carbon atoms, conjugated or nonconjugated dienes, polyenes, vinyl monomers and cyclic olefins. Non-limiting monomers useful in the invention may include norbornene, norbornadiene, isobutylene, isoprene, vinylbenzocyclobutane, styrenes, alkyl substituted styrene, ethylidene norbornene, dicyclopentadiene and cyclopentene.

In the most preferred embodiment of the process of the invention, a copolymer of ethylene is produced, where with ethylene, a comonomer having at least one alpha-olefin having from 4 to 15 carbon atoms, preferably from 4 to 12 carbon atoms, and most preferably from 4 to 8 carbon atoms, is polymerized in a gas phase process.

In another embodiment of the process of the invention, ethylene or propylene is polymerized with at least two different comonomers, optionally one of which may be a diene, to form a terpolymer.

In one embodiment, the invention is directed to a polymerization process, particularly a gas phase or slurry phase process, for polymerizing propylene alone or with one or more other monomers including ethylene, and/or other olefins having from 4 to 12 carbon atoms. Polypropylene polymers may be produced using the particularly bridged bulky ligands and metal compounds as described in U.S. Patent Nos. 5,296,434 and 5,278,264, both of which are herein incorporated by reference.

Typically in a gas phase polymerization process a continuous cycle is employed where in one part of the cycle of a reactor system, a cycling gas stream, otherwise known as a recycle stream or fluidizing medium, is heated in the reactor by the heat of polymerization. This heat is removed from the recycle composition in another part of the cycle by a cooling system external to the reactor. Generally,

in a gas fluidized bed process for producing polymers, a gaseous stream containing one or more monomers is continuously cycled through a fluidized bed in the presence of a catalyst under reactive conditions. The gaseous stream is withdrawn from the fluidized bed and recycled back into the reactor.

5 Simultaneously, polymer product is withdrawn from the reactor and fresh monomer is added to replace the polymerized monomer. (See for example U.S. Patent Nos. 4,543,399, 4,588,790, 5,028,670, 5,317,036, 5,352,749, 5,405,922, 5,436,304, 5,453,471, 5,462,999, 5,616,661 and 5,668,228, all of which are fully incorporated herein by reference.)

10 The reactor pressure in a gas phase process may vary from about 100 psig (690 kPa) to about 500 psig (3448 kPa), preferably in the range of from about 200 psig (1379 kPa) to about 400 psig (2759 kPa), more preferably in the range of from about 250 psig (1724 kPa) to about 350 psig (2414 kPa).

15 The reactor temperature in a gas phase process may vary from about 30°C to about 120°C, preferably from about 60°C to about 115°C, more preferably in the range of from about 70°C to 110°C, and most preferably in the range of from about 70°C to about 95°C.

20 Other gas phase processes contemplated by the process of the invention include series or multistage polymerization processes. Also gas phase processes contemplated by the invention include those described in U.S. Patent Nos. 5,627,242, 5,665,818 and 5,677,375, and European publications EP-A- 0 794 200 EP-B1-0 649 992, EP-A- 0 802 202 and EP-B- 0 634 421 all of which are herein fully incorporated by reference.

25 In a preferred embodiment, the reactor utilized in the present invention is capable and the process of the invention is producing greater than 500 lbs of polymer per hour (227 Kg/hr) to about 200,000 lbs/hr (90,900 Kg/hr) or higher of polymer, preferably greater than 1000 lbs/hr (455 Kg/hr), more preferably greater than 10,000 lbs/hr (4540 Kg/hr), even more preferably greater than 25,000 lbs/hr (11,300 Kg/hr), still more preferably greater than 35,000 lbs/hr (15,900 Kg/hr), 30 still even more preferably greater than 50,000 lbs/hr (22,700 Kg/hr) and most preferably greater than 65,000 lbs/hr (29,000 Kg/hr) to greater than 100,000 lbs/hr (45,500 Kg/hr).

35 A slurry polymerization process generally uses pressures in the range of from about 1 to about 50 atmospheres and even greater and temperatures in the range of 0°C to about 120°C. In a slurry polymerization, a suspension of solid,

particulate polymer is formed in a liquid polymerization diluent medium to which ethylene and comonomers and often hydrogen along with catalyst are added. The suspension including diluent is intermittently or continuously removed from the reactor where the volatile components are separated from the polymer and 5 recycled, optionally after a distillation, to the reactor. The liquid diluent employed in the polymerization medium is typically an alkane having from 3 to 7 carbon atoms, preferably a branched alkane. The medium employed should be liquid under the conditions of polymerization and relatively inert. When a propane medium is used the process must be operated above the reaction diluent 10 critical temperature and pressure. Preferably, a hexane or an isobutane medium is employed.

A preferred polymerization technique of the invention is referred to as a particle form polymerization, or a slurry process where the temperature is kept below the temperature at which the polymer goes into solution. Such technique is 15 well known in the art, and described in for instance U.S. Patent No. 3,248,179, which is fully incorporated herein by reference. Other slurry processes include those employing a loop reactor and those utilizing a plurality of stirred reactors in series, parallel, or combinations thereof. Non-limiting examples of slurry processes include continuous loop or stirred tank processes. Also, other examples 20 of slurry processes are described in U.S. Patent No. 4,613,484, which is herein fully incorporated by reference.

In an embodiment the reactor used in the slurry process of the invention is capable of and the process of the invention is producing greater than 2000 lbs of polymer per hour (907 Kg/hr), more preferably greater than 5000 lbs/hr (2268 25 Kg/hr), and most preferably greater than 10,000 lbs/hr (4540 Kg/hr). In another embodiment the slurry reactor used in the process of the invention is producing greater than 15,000 lbs of polymer per hour (6804 Kg/hr), preferably greater than 25,000 lbs/hr (11,340 Kg/hr) to about 100,000 lbs/hr (45,500 Kg/hr).

Examples of solution processes are described in U.S. Patent Nos. 30 4,271,060, 5,001,205, 5,236,998 and 5,589,555, which are fully incorporated herein by reference

A preferred process of the invention is where the process, preferably a slurry or gas phase process is operated in the presence of the catalyst composition of the invention and in the absence of or essentially free of any scavengers, such 35 as triethylaluminum, trimethylaluminum, tri-isobutylaluminum and tri-n-

hexylaluminum and diethyl aluminum chloride, dibutyl zinc and the like. This preferred process is described in PCT publication WO 96/08520 and U.S. Patent No. 5,712,352 and 5,763,543, which are herein fully incorporated by reference.

### **Polymer Products**

5 The polymers produced by the process of the invention can be used in a wide variety of products and end-use applications. The polymers produced by the process of the invention include linear low-density polyethylene, elastomers, plastomers, high-density polyethylenes, low-density polyethylenes, polypropylene and polypropylene copolymers.

10 The polymers, typically ethylene based polymers, have a density in the range of from 0.86g/cc to 0.97 g/cc, preferably in the range of from 0.88 g/cc to 0.965 g/cc, more preferably in the range of from 0.900 g/cc to 0.96 g/cc, even more preferably in the range of from 0.905 g/cc to 0.95 g/cc, yet even more preferably in the range from 0.910 g/cc to 0.940 g/cc, and most preferably greater than 0.915 g/cc, preferably greater than 0.920 g/cc, and most preferably greater than 0.925 g/cc. Density is measured in accordance with ASTM-D-1238.

15 The polymers produced by the process of the invention typically have a molecular weight distribution, a weight average molecular weight to number average molecular weight ( $M_w/M_n$ ) of greater than 1.5 to about 15, particularly greater than 2 to about 10, more preferably greater than about 2.2 to less than about 8, and most preferably from 2.5 to 8.

20 Also, the polymers of the invention typically have a narrow composition distribution as measured by Composition Distribution Breadth Index (CDBI). Further details of determining the CDBI of a copolymer are known to those skilled in the art. See, for example, PCT Patent Application WO 93/03093, published February 18, 1993, which is fully incorporated herein by reference.

25 The bulky ligand metallocene catalyzed polymers of the invention in one embodiment have CDBI's generally in the range of greater than 50% to 100%, preferably 99%, preferably in the range of 55% to 85%, and more preferably 60% to 80%, even more preferably greater than 60%, still even more preferably greater than 65%.

30 In another embodiment, polymers produced using a bulky ligand metallocene catalyst system of the invention have a CDBI less than 50%, more preferably less than 40%, and most preferably less than 30%.

The polymers of the present invention in one embodiment have a melt index (MI) or ( $I_2$ ) as measured by ASTM-D-1238-E in the range from 0.01 dg/min to 1000 dg/min, more preferably from about 0.01 dg/min to about 100 dg/min, even more preferably from about 0.1 dg/min to about 50 dg/min, and most 5 preferably from about 0.1 dg/min to about 10 dg/min.

The polymers of the invention in an embodiment have a melt index ratio ( $I_{21}/I_2$ ) ( $I_{21}$  is measured by ASTM-D-1238-F) of from 10 to less than 25, more preferably from about 15 to less than 25.

The polymers of the invention in a preferred embodiment have a melt 10 index ratio ( $I_{21}/I_2$ ) ( $I_{21}$  is measured by ASTM-D-1238-F) of from preferably greater than 25, more preferably greater than 30, even more preferably greater than 40, still even more preferably greater than 50 and most preferably greater than 65. In an embodiment, the polymer of the invention may have a narrow molecular weight distribution and a broad composition distribution or vice-versa, and may 15 be those polymers described in U.S. Patent No. 5,798,427 incorporated herein by reference.

In yet another embodiment, propylene based polymers are produced in the process of the invention. These polymers include atactic polypropylene, isotactic polypropylene, hemi-isotactic and syndiotactic polypropylene. Other propylene 20 polymers include propylene block or impact copolymers. Propylene polymers of these types are well known in the art see for example U.S. Patent Nos. 4,794,096, 3,248,455, 4,376,851, 5,036,034 and 5,459,117, all of which are herein incorporated by reference.

The polymers of the invention may be blended and/or coextruded with any 25 other polymer. Non-limiting examples of other polymers include linear low density polyethylenes produced via conventional Ziegler-Natta and/or bulky ligand metallocene catalysis, elastomers, plastomers, high pressure low density polyethylene, high density polyethylenes, polypropylenes and the like.

Polymers produced by the process of the invention and blends thereof are 30 useful in such forming operations as film, sheet, and fiber extrusion and co-extrusion as well as blow molding, injection molding and rotary molding. Films include blown or cast films formed by coextrusion or by lamination useful as shrink film, cling film, stretch film, sealing films, oriented films, snack packaging, heavy duty bags, grocery sacks, baked and frozen food packaging, medical 35 packaging, industrial liners, membranes, etc. in food-contact and non-food contact

applications. Fibers include melt spinning, solution spinning and melt blown fiber operations for use in woven or non-woven form to make filters, diaper fabrics, medical garments, geotextiles, etc. Extruded articles include medical tubing, wire and cable coatings, geomembranes, and pond liners. Molded articles include 5 single and multi-layered constructions in the form of bottles, tanks, large hollow articles, rigid food containers and toys, etc.

### **EXAMPLES**

In order to provide a better understanding of the present invention 10 including representative advantages thereof, the following examples are offered.

Activity values in Table 1 are normalized values based upon grams of polymer produced per mmol of transition metal in the catalyst per hour per 100 psi (690 kPa) of ethylene polymerization pressure. MI is Melt Index, and was reported as grams per 10 minutes per ASTM D-1238, Condition E. FI is Flow 15 Index, and was measured 10 times the weight used in the melt index above per ASTM D-1238, Condition F. MFR is Melt Flow Ratio, and is the ratio of FI:MI.

MAO is methylalumoxane in toluene (30 wt%), available from Albemarle Corporation, Baton Rouge, Louisiana.

Kaydol, a white mineral oil, was purchased from Witco Corporation, 20 Memphis, Tennessee, and was purified by first degassed with nitrogen for 1 hour, followed by heating at 80°C under vacuum for 10 hours.

BBF is butyl branch frequency of hexene-1/ethylene copolymer as was measures on a Bruker AC 300 NMR spectrometer. All C<sup>13</sup> NMR experiments are done under Nuclear Overhouser Effect (NOE) conditions using a 30° pulse width 25 and a repetition time of five (5) seconds. BBF are calculated in number of branches per 1000 backbone carbon atoms using standard assignments as is well known in the art.

BF-20 is dimethylanilinium tetrakis(pentafluorophenyl) borate and is available from Boulder Scientific Company, Mead, Colorado.

30 **Example 1**

**Preparation of Supported Activator**

A toluene solution of methylalumoxane (MAO) was prepared by mixing 960 g of 30 wt% MAO, (MAO was purchased from Albemarle Corporation, Baton Rouge, Louisiana), in 2.7 liter of dry, degassed toluene. This solution was 35 stirred at ambient temperature while 850 g of silica gel (Davison 955, dehydrated

at 600°C available from W.R. Grace, Davison Division, Baltimore, Maryland) was added. The resulting slurry was stirred at ambient temperature for 1 hour and the solvent was removed under reduced pressure with a stream of nitrogen at 85°C. The drying is continued until the material temperature has been constant for 2 hours. The resulting free-flowing white powder has an aluminum loading of 4.3 mmol Al per gram of solid.

The following are represented examples of forming the Group 15 containing transition metal catalyst compound of the invention. Furthermore, the two catalyst compounds used in the polymerization below are available from 10 Albemarle Corporation, Baton Rouge, Louisiana.

**Example 2**

**Preparation of [(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)NHC<sub>2</sub>CH<sub>2</sub>]<sub>2</sub>NH (Ligand)**

A 2 L one-armed Schlenk flask was charged with a magnetic stir bar, diethylenetriamine (23.450 g, 0.227 mol), mesityl bromide (90.51 g, 0.455 mol), 15 tris(dibenzylideneacetone)dipalladium (1.041 g, 1.14 mmol), racemic-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (2.123 g, 3.41 mmol), sodium tert-butoxide (65.535 g, 0.682 mol), and toluene (800 mL). The reaction mixture was heated to 95°C and stirred. After 4 days the reaction was complete, as judged by proton NMR spectroscopy. All solvent was removed under vacuum and the 20 residues dissolved in diethyl ether (1 L). The ether was washed three times with water (1 L) and saturated aqueous NaCl (500 mL) and dried over magnesium sulfate. Removal of the ether in vacuo yielded a red oil which was dried at 70°C for 12 h under vacuum (yield: 71.10 g, 92%). <sup>1</sup>H NMR δ 6.83 (s, 4), 3.39 (br s, 2), 2.86 (t, 4), 2.49 (t, 4), 2.27 (s, 12), 2.21 (s, 6), 0.68 (br s, 1). <sup>13</sup>C NMR δ 25 143.74, 131.35, 129.83, 129.55, 50.17, 48.56, 20.70, 18.51.

**Example 2A**

**Preparation of [(2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)NHC<sub>2</sub>CH<sub>2</sub>]<sub>2</sub>NH}Hf(CH<sub>2</sub>Ph)<sub>2</sub> (Hf-HN3)**

A 250 mL round bottom flask was charged with a magnetic stir bar, tetrabenzyl hafnium (4.063 g, 7.482 mmol), and 150 mL of toluene under dry, 30 oxygen-free nitrogen. Solid triamine ligand above (2.545 g, 7.495 mmol) was added with stirring over 1 minute (the desired compound precipitates). The volume of the slurry was reduced to 30 mL and 120 mL of pentane added with stirring. The solid pale yellow product was collected by filtration and dried under vacuum (4.562 g, 87% yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ 7.21-6.79 (m, 12), 6.16 (d, 2),

3.39 (m, 2), 3.14 (m, 2), 2.65 (s, 6), 2.40 (s, 6), 2.35 (m, 2), 2.23 (m, 2), 2.19 (s, 6) 1.60 (s, 2), 1.26 (s, 2), NH obscured.

**Example 2B**

**Preparation of  $\{[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)\text{NCH}_2\text{CH}_2]_2\text{NH}\}\text{Zr}(\text{CH}_2\text{Ph})_2$  (Zr-HN3)**

5 A 500 mL round bottom flask was charged with a magnetic stir bar, tetrabenzyl zirconium (41.729 g, 91.56 mmol), and 300 mL of toluene under dry, oxygen-free nitrogen. Solid triamine ligand above (32.773 g, 96.52 mmol) was added with stirring over 1 minute (the desired compound precipitates). The 10 volume of the slurry was reduced to 100 mL and 300 mL of pentane added with stirring. The solid yellow-orange product was collected by filtration and dried under vacuum (44.811 g, 80% yield).  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.22-6.81 (m, 12), 5.90 (d, 2), 3.38 (m, 2), 3.11 (m, 2), 3.01 (m, 1), 2.49 (m, 4), 2.43 (s, 6), 2.41 (s, 6), 2.18 (s, 6), 1.89 (s, 2), 0.96 (s, 2).

15 For purposes of the Table below Catalyst Compound A is Bis(2,4,6-trimethylphenyl amido ethyl)amine hafnium dibenzyl and Catalyst Compound B is Bis(2,4,6-trimethylphenyl amido ethyl)amine zirconium dibenzyl.

**Example 3**

**Preparation of Catalyst System I**

To a Kaydol oil solution of bisamide hafnium compound (Catalyst Compound A, 0.032 g, 0.0459 mmol in 8 g of Kaydol oil) were added to the supported activator prepared in Example 1 above (1.35 g). The resulting slurry, slurried catalyst system, was then stirred for 16 hours at room temperature before being used for 25 polymerization.

**Example 4**

**Preparation of Catalyst System II**

To a Kaydol oil solution of bisamide zirconium compound (Catalyst Compound B, 0.025 g, 0.0410 mmol in 15 g of Kaydol oil) were added to the supported activator prepared in Example 1 above (1.35 g). The resulting slurry, slurried catalyst system, was then stirred for 16 hours at room temperature before being used for polymerization.

As described previously in this patent specification there are various methods for adding the ionizing activator. The following non-limiting examples exemplify the various embodiments methods of the invention.

**Example 5****Methods for Introducing the Ionizing Activator****Method 1**

In Method 1, the ionizing activator, the BF-20 compound described above, 5 Catalyst Compound A or B, and the supported activator were all mixed at the same time in Kaydol oil. The resulting mixture was then stirred at room temperature for 16 hours before the catalyst composition of the invention is employed for polymerization.

**Method 2**

10 In Method 2, the Catalyst Compound A or B is mixed with the supported activator first to form Catalyst System I or II, a slurried catalyst system in Kaydol oil. Then, the ionizing activator was added directly to Catalyst System I or II. The resulting mixture, catalyst composition of the invention, was then stirred at room temperature for 16 hours before being employed for polymerization.

**Method 3**

15 In Method 3 the ionizing activator, the BF-20 compound, was mixed with a Kaydol oil slurry of the supported activator. This ionizing activator/supported activator mixture was then stirred at room temperature for 16 hour before Catalyst Compound A or B was added. The resulting mixture was then stirred for another 20 16 hours before being used for polymerization.

**Example 6 through 16 and Comparative Examples C1-C5****Polymerization Process**

In each of Examples 6 through 16 and Comparative Examples C1 through C5, polyethylene was produced in a slurry phase reactor using the catalyst 25 composition as specified in Table 1 and the polymerization process described below. For each of Examples 6 through 16, a slurry using one of the Methods 1, 2 or 3 as described above was prepared. A sample of each of the slurried catalyst compositions prepared using Method 1, 2 or 3 was added to an 8 ounce (250 ml) bottle containing 100 ml of hexane. (In Examples 6 though 8 and 13 and 14, 30 Catalyst System I or II is used and in Example 9 through 12 and 15 and 16, Catalyst Compounds A or B is used.) A sample of each of Catalyst System I or II was used in the Comparative Examples C1 through C5 and as identified in Table 1. Hexene-1 comonomer was added to the catalyst compositions. Anhydrous conditions were maintained. The following describes the polymerization process 35 used for Examples 6 through 16 and Comparative Examples C1 through C5.

The slurry reactor was a 1 liter, stainless steel autoclave equipped with a mechanical agitator. The reactor was first dried by heating at 95°C under a stream of dry nitrogen for 40 minutes. After cooling the reactor to 50°C, 500 ml of 5 hexane was added to the reactor, followed by 0.25 ml of tri-isobutylaluminum (TIBA) in hexane (0.86 mole, used as scavenger), and the reactor component was stirred under a gentle flow of nitrogen. The catalyst composition of the invention, or the compositions in the comparative examples (where no ionizing activator was used), was then transferred to the reactor under a stream of nitrogen and the 10 reactor was sealed. The temperature of the reactor was gradually raised to 75°C and the reactor was pressured to 150 psi (1034 kPa) with ethylene. Heating was continued until a polymerization temperature of 85°C was attained. Unless otherwise noted, polymerization was continued for 30 minutes, during which time ethylene was continually added to the reactor to maintain a constant pressure. At 15 the end of 30 minutes, the reactor was vented and opened.

**Table 1**

Example	Catalyst	Ionizing Activator <sup>1</sup>	Method	1-Hexene (ml)	Activity	FI	BBF
C1	I	--	--	0	17731	no flow	--
C2	I	--	--	20	16191	0.2	15.3
C3	I	--	--	60	12008	1.6	42.9
6	I	0.54	2	0	26821	no flow	--
7	I	0.54	2	20	38011	3.1	--
8	I	0.54	2	60	55920	7.2	--
9	A	0.3	1	0	25037	no flow	--
10	A	0.3	1	20	40827	3.8	46.5
11	A	0.3	1	60	65413	20	86.6
12	A	0.59	3	60	66917	14	--
C4	II	--	--	20	38391	no flow	--
C5	II	--	--	60	39714	no flow	--
13	II	0.7	2	20	43534	no flow	--
14	II	0.7	2	60	54737	no flow	--
15	B	0.7	1	20	43819	no flow	--
16	B	0.7	1	60	54376	no flow	--

<sup>1</sup> The mole ratio of the ionizing activator to the metal of the Group 15 transition metal compound.

While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will appreciate that the invention lends itself to variations not necessarily illustrated herein. For example, 10 it is contemplated that two or more supported activators, and two or more Group 15 catalyst compounds are used in a mixture with one or more ionizing activators. It is also contemplated that in this embodiment, that the supported activators may be the same or different. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present 15 invention.

**CLAIMS**

We Claim:

1. A method for preparing a catalyst composition comprising the steps of:
  - (a) forming a supported activator;
  - (b) introducing a Group 15 containing transition metal catalyst compound; and
  - (c) introducing an ionizing activator.
2. The method of claim 1 wherein the supported activator is combined with the Group 15 containing transition metal catalyst compound in a liquid prior to introducing the ionizing activator.
3. The method of claim 1 wherein the supported activator comprises a support material and an activator.
4. The method of claim 3 wherein the activator is an alumoxane.
5. The method of claim 1 wherein the supported activator is in a mineral oil.
6. The method of claim 1 wherein the ionizing activator is a Group 13 metal containing activator.
7. The method of claim 1 wherein the supported activator is the reaction product of a support material comprising surface hydroxyl groups and an organoaluminum compound.
8. The method of claim 1 wherein the Group 15 containing transition metal compound is a Group 15 containing bidentate or tridentate ligated transition metal catalyst compound.
9. The method of claim 1 wherein the Group 15 containing transition metal compound has a transition metal bound to at least one leaving group and also bound to at least two Group 15 atoms, at least one of which is also bound to a Group 15 or 16 atom through another group.

10. A process for polymerizing olefin(s) in the presence of a catalyst composition of a supported activator, a Group 15 containing transition metal catalyst compound, and ionizing activator.
11. The process of claim 10 wherein the process is a gas phase process.
12. The process of claim 10 wherein the supported activator comprises a support material and an activator.
13. The process of claim 10 wherein the catalyst composition is in a slurry state.
14. The process of claim 10 wherein the Group 15 containing transition metal catalyst compound is a Group 15 containing bidentate or tridentate ligated transition metal catalyst compound.
15. An activated olefin polymerization catalyst composition comprising supported activator, a Group 15 containing bidentate or tridentate ligated transition metal catalyst compound, and an ionizing activator.
16. The catalyst composition of claim 15 wherein the supported activator comprises a support material and an activator.
17. The catalyst composition of claim 15 wherein the catalyst composition is in a slurry state.
18. The catalyst composition of claim 17 wherein the catalyst composition is slurried in mineral oil.
19. The catalyst composition of claim 15 wherein the supported activator is supported alumoxane.
20. The catalyst composition of claim 15, wherein the ionizing activator is ionic.

21. The catalyst composition of claim 15 wherein the mole ratio of the metal of the ionizing activator to the transition metal of the Group 15 containing transition metal catalyst compound is from 0.1 to 0.9.

**A METHOD FOR PREPARING A CATALYST  
COMPOSITION AND ITS USE IN A POLYMERIZATION PROCESS**

**ABSTRACT**

5

The present invention relates to a catalyst composition of a supported activator, a catalyst compound and an ionizing activator and its use in a process for polymerizing olefin(s). The invention is also directed to a method for making the catalyst composition above.

10

**"PATENT"****DECLARATION FOR PATENT APPLICATION**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

**A Method for Preparing a Catalyst Composition and Its Use in a Polymerization Process**

the specification of which is attached hereto unless the following box is checked:

[X] was filed on November 16, 2000 as Application Serial No. or PCT International Application No. 2000U032.US  
and was amended on N/A (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate(s), or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application(s) for patent or inventor's certificate(s), or PCT International application having a filing date before that of the application on which priority is claimed.

**Prior Foreign Application(s)****Priority Claimed**

<u>  </u> [ ] (Number)	<u>  </u> [ ] (Country)	<u>  </u> [ ] (Day/Month/Year Filed)	<u>  </u> [ ] Yes	<u>  </u> [ ] No
<u>  </u> [ ] (Number)	<u>  </u> [ ] (Country)	<u>  </u> [ ] (Day/Month/Year Filed)	<u>  </u> [ ] Yes	<u>  </u> [ ] No

I hereby claim the benefit under 35 U.S.C. § 119(e)(1)-(2) of any United States provisional application(s) listed below.

<u>  </u> [ ] (Application Number)	<u>  </u> [ ] (Filing Date)
<u>  </u> [ ] (Application Number)	<u>  </u> [ ] (Filing Date)

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose material information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

<u>  </u> [ ] (Application Serial No.)	<u>  </u> [ ] (Filing Date)	<u>  </u> [ ] (Status - patented, pending, abandoned)
<u>  </u> [ ] (Application Serial No.)	<u>  </u> [ ] (Filing Date)	<u>  </u> [ ] (Status - patented, pending, abandoned)

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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